HHS Public Access

Author manuscript

J Occup Environ Hyg. Author manuscript; available in PMC 2015 September 28.

Published in final edited form as:

J Occup Environ Hyg. 2014 ; 11(8): 547–555. doi:10.1080/15459624.2014.880444.

Exposure to Chlorpyrifos in Gaseous and Particulate Form in Greenhouses: A Pilot Study

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Abstract

Phase distribution of airborne chemicals is important because intake and uptake mechanisms of each phase are different. The phase distribution and concentrations are needed to determine strategies of exposure assessment, hazard control, and worker protection. However, procedures for establishing phase distribution and concentration have not been standardized. The objective of this study was to compare measurements of an airborne semivolatile pesticide (chlorpyrifos) by phase using two different procedures. Six pesticide applications in two facilities were studied and at each site, samples were collected for three time slots: T1, the first 1 or 2 hr after the commencement of application; T2, a 6-hr period immediately following T1; and T3, a 6-hr period after the required reentry interval (24 hr for chlorpyrifos). Two phase-separating devices were co-located at the center of each greenhouse: semivolatile aerosol dichotomous sampler (SADS) using flow rates of 1.8 $l.min^{-1}$ and 0.2 $l.min^{-1}$, corresponding to a total inlet flow rate of 2.0 $l.min^{-1}$ with a vapor phase flow fraction of 0.1; and an electrostatic precipitator (ESP), along with a standard OVS XAD-2 tube. Chlorpyrifos in vapor and particulate form in a SADS sampling train and that in vapor form in an ESP sampling train were collected in OVS tubes. Chlorpyrifos in particulate form in the ESP setting would have been collected on aluminum substrate. However, no chlorpyrifos in particulate form was recovered from the ESP. Overall (vapor plus particle) concentrations measured by OVS ranged 11.7 – 186.6 $\mu g/m^3$ at T1 and decreased on average 77.1% and 98.9% at T2 and T3, respectively. Overall concentrations measured by SADS were 66.6%, 72.7%, and 102% of those measured by OVS on average at T1, T2, and T3, respectively. Particle fractions from the overall concentrations measured by SADS were 60.0%, 49.2%, and 13.8%, respectively, for T1, T2, and T3. SADS gives better guidance on the distribution of chlorpyrifos than does the ESP, although the accuracy of the concentration distribution cannot be verified in the absence of a standardized procedure for determining phase division.

Keywords

air sampling; chlorpyrifos; greenhouse; pesticide; semi-volatile organic compound

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INTRODUCTION

Information on phase distribution of airborne semivolatile organic compounds (SVOCs) is important in occupational health because of the difference in the intake and uptake mechanisms of the two phases. Particle deposition in the lungs is a function of aerodynamic diameter, whereas gas deposition is a function of tissue solubility, which is related to the air-lung partitioning ratio.[1] In the case of semi-volatile chemicals, mass distributes between the two phases according to a gas-particle partitioning ratio.

Many chemicals tend to be distributed between the particle and vapor phases in workplaces. Since 2000, the American Conference of Governmental Industrial Hygienists (ACGIH®) has added an IFV (inhalable fraction and vapor) notation for chemicals that need to be evaluated for both inhalable fraction and vapor due to their volatility. The Threshold Limit Value (TLV®) list for 2012 includes 55 chemicals having this notation not including the 4 chemicals on the Notice of Intended Change. Most of them can be classified as semivolatile chemicals and a few as volatile chemicals, according to their vapor pressures. Pesticides make up over 70% of TLVs having an IFV notation.[2] Control methods for each phase including personal protection equipment are fundamentally different. Filtration for particles and adsorption for vapor molecules has been commonly considered as an economic control method, but it has been less than successful in controlling SVOCs.

Agricultural workers are at risk from exposure to pesticides when working in different crop categories. The Department of Labor estimates that approximately 1.8 million workers perform hired agricultural crop work in the United States.[3]The National Center for Food and Agricultural Policy (NCFAP) reported pesticide use in U.S. crop production for 1997 by their active ingredients.[4]The amount of semivolatile insecticides (based on the vapor pressures of active ingredients) used in the United Sates was estimated to be ca.50×10^6 pounds of active ingredients and over 95 percent of the semivolatile insecticides had TLVs. The upper and lower cut-off of vapor pressures for SVOC were 10^{-4}atm and 10^{-11}atm, respectively.[5] This report has not been updated since 1997.

Almost all pesticides having Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs) are covered by National Institute for Occupational Safety and Health (NIOSH) Sampling and Analytical Methods #5600 for Organophosphorus Pesticides and # 5601 for Organonitrogen Pesticides, which list 19 and 15 chemicals, respectively, under each method. All of those chemicals, except one solid pesticide, belong to SVOCs according to their vapor pressures reported in the methods or in their Material Safety Data Sheets (MSDSs).[6,7] Most TLVs or PELs for organophosphorus pesticides are lower than 1.0 mg/m^3, indicating a potentially high toxicity.

Inhalation exposure of pesticides is important even considering that other routes of exposure are often considered to contribute up to 80% of total pesticide exposure.[8] Durham and Wolfe[9] suggested the “more rapid and more complete absorption of toxicant drawn into the lungs as compared with that deposited on the skin.” In many studies the absorption of the respiratory dose has been considered as 100%, while that of the dermal dose has been considered 10% or lower.[9–12] In some special environments such as the inside of

greenhouses or storage buildings where mixing and loading happen, inhalation exposure can be more important due to greater confinement compared to the outdoor situation. Aprea et al.[13] reported that depending on their tasks the respiratory dose of workers during industrial formulation was several times higher than skin contamination. Dowling and Seiber[8] emphasized the importance of respiratory exposure to pesticides among agricultural populations. Their study identified some high risk activities of application of high volatility soil fumigants, where respiratory exposures are important, including handling volatile liquid pesticides for mixers and loaders, elevated track boom application, and greenhouse applications. In the National Agricultural Workers Survey,[14] depending on the size of farms, 4.5–25.1% of farmworkers whose primary occupation is working in the field on tasks like harvesting and weeding have experienced loading, mixing, or application of pesticides in the last 12 months.

Few devices are available to evaluate the phase distributions of semivolatile chemicals. Several different types of sampling devices are available to evaluate concentrations of aerosols. Popular sampling methods for chemicals in the particle phase include impingers, filters, electrostatic precipitators (ESPs), impactors, and virtual impactors. Many of these methods have been shown to be subject to evaporative losses when used to collect SVOCs.[1,15,16] Depending on the principles of the sampling mechanism, some methods are more subject to evaporative loss than others. Several different types of sampling devices are available to evaluate concentrations of chemicals in vapor form. Sorbent tubes are most widely used to collect chemical vapors and will also sample some, but not all, particles. Devices sampling only one phase are therefore not appropriate for measuring semivolatile aerosols due to the characteristics of SVOCs described previously. Portability of sampling instruments is also a consideration for personal exposure assessment.

Kim and Raynor[17] developed a Semivolatile Aerosol Dichotomous Sampler (SADS)). The SADS works as a preseparator similar to cyclones. The SADS is a round nozzle virtual impactor having an inverted flow ratio, which changes the airflow through the sampler and the trajectories of some particles relative to the traditional virtual impactor flow settings. The 50% cutsize of the SADS was optimized in previous experiments at 0.25 μm aerodynamic equivalent diameter when the total inlet flow rate was set to 2.0 l.min^{-1} and 0.2 l.min^{-1} for the vapor flow (flow fraction 0.1).[18]Any collection media designed for active air movement can be utilized to sample the SVOCs of interest. SADS was tested in laboratory settings for oil mists and worked well.[19]Separation of particles from aerosols using SADS minimizes evaporative loss during sampling and the apparatus is less affected by temporal variation of the phase distributions. The SADS was designed for personal sampling and optimized to accommodate the pressure drops typically encountered with sampling media. The SADS also does not require electrical power to separate particles and can be easily utilized for personal sampling. This feature also lowers the cost for fabrication.

Many semivolatile pesticides can be sampled with OSHA versatile sampler (OVS) tubes.[20,21] OVS tubes are not subject to evaporative loss during sampling because of the presence of sorbent media after the filter. Thus the structure of the OVS tube allows for simultaneous collection of aerosol and vapors. However, even if the media were analyzed separately, it is unlikely that accurate phase information can be obtained using this method

and thus the media is not separated for analysis. Note that while OSHA requires glass fiber filters, NIOSH requires quartz filters in their similar procedure. A thorough evaluation of the particle size-selection efficiency of the OVS tube has not been published.

Table I is a summary of semivolatile pesticides exposure studies performed in greenhouses. Few studies have obtained data on phase distribution. Siebers and Mattusch [23] did some additional sampling using glass fiber filters in front of the Tenax tubes. While parathion was mainly detected in the Tenax tubes (>95%), pirimicarb was found at an average of 65% in the filter and 35% in the Tenax tube. It seems the vapor pressures of two active ingredients, 5.0×10^{-8}atm@20°C and 3.0×10^{-8}atm@20°C, respectively, cannot explain these results thoroughly.

The overall objective of this pilot study was to assess exposures to an airborne semivolatile pesticide (chlorpyrifos) in greenhouses according to its phase profile. The specific aim of this study was to compare available methods for selection of an appropriate method that would determine phase information to evaluate phase distributions of airborne chlorpyrifos in greenhouses. A secondary aim, to survey the factors affecting phase distributions in greenhouses, will require further investigations, but some discussion of these factors is included.

METHODS

Static area sampling was performed inside of greenhouses. Sampling sites were two greenhouses in research facilities located in Minnesota and Maryland, which are noted as MN and MD in Table II. The square footage areas of MN and MD were 750 ft^2 and 2,990 ft^2, respectively. Air samples were collected during summer 2010 and 2011. Plants were growing in pots and located two feet above the ground in site MN and on the ground in site MD. The height of plants was on average 4 feet and 6 feet in site MN and site MD, respectively. The distance between plant pots was approximately 1 foot.

For each site, samples were collected for three time slots: T1, the first 1 or 2 hr after the commencement of application; T2, a 6-hr period immediately following T1; and T3, a 6-hr period after the required re-entry interval (24 hr for chlorpyrifos). T1 was a duration of 1 hr in 2010. After finding the amounts of chlorpyrifos collected were below limit of detection (LOD), T1 was increased to 2 hr in 2011. The duration of T2 and T3 was 6 hr in all visits (Figure 1).

Airborne chlorpyrifos concentrations were measured by three different methods: SADS, electrostatic precipitator (ESP), and NIOSH standard method (OSHA versatile sampler (OVS) tube containing Amberlite XAD-2 sorbent resin in combination with polyurethane foam and a pre-filter). Five optimized SADS were machined from aluminum and used throughout this study. XAD-2 OVS sorbent tubes (226–58A, SKC Inc., Eighty Four, Pa) were attached to the two outlets of the SADS to act as collection media for the vapor flow and the particle flow. The SADS mounted with sampling media was connected to a vacuum pump (Gast, Benton Harbor, Mich.). The flow rates for the vapor and particle outlets were 0.2 and 1.8 $l.min^{-1}$, respectively, to give a total flow rate of 2.0 $l.min^{-1}$ and a vapor flow

fraction of 0.1 of the total, per previous studies.[18,19] Flow rates were maintained by two mass flow controllers (GFC17, Aalborg Instruments & Controls, Inc., Orangeburg, N.Y.).

Another sampling train was the ESP with a XAD-2 OVS tube. An ESP (Aerosol Associates, Chapel Hill, N.C.) developed for personal sampling, which is reported to have less evaporative loss than filtration methods, was used to sample both phases.[16] A rectangular sheet of aluminum foil measuring 4 cm by 4 cm, was coiled inside the aluminum tube provided by the manufacturer to act as the substrate for particulate collection. A XAD-2 OVS tube was connected in series to the outlet of the ESP to collect vapor and any uncollected particulate. This sampling train was connected to the same vacuum pump to which the SADS was connected. The flow rate for the ESP was 1.0 $l.min^{-1}$ and was controlled by a mass flow controller (GFC17, Aalborg Instruments & Controls, Inc., Orangeburg, N.Y.).

XAD-2 OVS tubes (226–58A, SKC Inc., Eighty Four, Pa.) also were used as a control to sample the total pesticide (vapor plus aerosol) independently. The sampling flow rate was 1.0 $l.min^{-1}$ and was controlled by a mass flow controller (GFC17, Aalborg Instruments & Controls, Inc., Orangeburg, N.Y.).

An Aerosol Particle Sizer (Model 3321, TSI Inc., Shoreview, Minn.) was used to monitor the number concentration and the size distribution of particles. The APS provides real-time aerodynamic measurements of particles between 0.5 μm and 20 μm aerodynamic equivalent diameter and in this range the size distribution was evaluated as log-normal. Temperature and humidity inside greenhouses were recorded using a Temperature Humidity USB Data Logger (THL1, Universal Enterprise Inc., Beaverton, Ore.) during sampling. The APS data and temperature/humidity were automatically logged per minute.

Mass flow controllers for three samplers and the APS were placed inside a purpose-built chamber sitting on top of a cart to prevent the surface of the devices from being contaminated by pesticides during sampling. The chamber was built from plastic panels and an aluminum frame. The sampling inlet of the APS was open to the top of the sampling cart and the exhaust air was vented to the outside of the chamber. The vacuum pump was outside the chamber. The temperature in the chamber was monitored using the same temperature/humidity logger. Three samplers were mounted on a horizontal rig located next to the sampling cart and connected to the mass flow controllers using Tygon tubing and quick disconnect couplings.

Both ends of the XAD-2 OVS tubes were capped and the tubes were shipped to the NIOSH contract laboratory for analysis. The aluminum substrates mounted in the ESP were immediately separated from the ESP after each sampling period and were placed into 8.75 mm × 50 mm test tubes (with screw caps) containing extraction solution (90% toluene and 10% acetone). After capping tightly, the test tubes were agitated vertically by hand for 20 sec and were shipped along with XAD-2 OVS tubes to the contract laboratory for analysis.

Calculation of Concentrations

The concentrations of chlorpyrifos in each phase were calculated using the equations described by Kim and Raynor.[19] The mass collected on each OVS tube attached to the particle flow side (M_{OVSp}) of the SADS includes both particle mass and mass collected from the vapor-phase (and thus the vapor phase mass must be subtracted from the total to obtain the particle mass in equation 2). This mass, and the mass of vapor only from the vapor flow side (M_{OVSv}) were obtained from analytical report. Sampling time (t) and each flow rate (Q_{vapor} and $Q_{particle}$) were recorded on sampling sheets. The airborne vapor concentration (C_{vapor}), the airborne particle concentration ($C_{particle}$), the overall concentration ($C_{overall}$), and the fraction of particle concentration ($f_{particle}$) can be determined using the following equations, under the assumption of complete particle separation:

$$C_{vapor} = \frac{M_{OVSv}}{t \times Q_{vapor}} \quad (1)$$

$$C_{particle} = \frac{M_{OVSp} - \left(\frac{Q_{particle}}{Q_{vapor}}\right) \times M_{OVSv}}{t \times (Q_{vapor} + Q_{particle})} \quad (2)$$

$$C_{overall} = \frac{M_{OVSp} + M_{OVSv}}{t \times (Q_{vapor} + Q_{particle})} \quad (3)$$

$$f_{particle} = \frac{C_{particle}}{C_{vapor} + C_{particle}} \quad (4)$$

RESULTS

Overall

Table III shows the overall concentrations of chlorpyrifos by sampling method and by sampling time slot scheme. After Visits 1 and 2, the ESP method was dropped since no chlorpyrifos was recovered from the substrates installed inside the ESP and only small amounts were recovered from OVS tubes connected to the outlet of the ESP in series. $C_{overall}$ measured by the independent XAD-2 OVS tubes and the XAD-2 OVS tubes attached to the SADS decreased over time. $C_{overall}$ for the XAD-2 OVS tubes decreased 77.1% and 98.9% on average at T2 and T3, respectively. Overall concentrations measured by XAD-2 OVS tubes attached to the SADS were 66.6%, 72.7%, and 102% of those measured by the independent XAD-2 OVS tubes on average at T1, T2, and T3, respectively. The results from the two methods were compared by paired-t test and there was a significant difference at T1 ($p<0.05$), but not at T2 or T3 ($P>0.05$). However, the small number of data points which are not normally distributed may invalidate the use of the t-test in determining significance of differences.

Phase Distribution

The airborne vapor concentration (C_{vapor}), the airborne particle concentration ($C_{particle}$), the overall concentration ($C_{overall}$), and the fraction of particle concentration ($f_{particle}$) for each visit are summarized in Table IV. For Visit 1 and 2, $f_{particle}$ was not available because the mass collected on vapor flow side were below the detection limit. Although the detection limit could be used to estimate results, the outcome would be negative particle mass concentrations at T2 and T3. Except during T2 of Visit 5, the fractions of particle concentration decreased as time passed.

Particle Size Distribution

Figure 2 shows typical changes of particle size distribution before and after pesticide application. Because of preparation activities before pesticide application and door opening, the particle concentrations and size distributions were possibly close to those of outdoor air. During the pesticide application, the number median diameter was 1.0 μm with geometric standard deviation (GSD) = 1.6 and the total number concentration was approximately 7,000 #/cc. Particle concentration decreased below outdoor air level after the application was over and the door was closed.

Temperature and Relative Humidity

The ranges of temperature inside the greenhouses during each visit are listed in Table II. Average temperature and relative humidity during sampling were 91.7°F and 59.0%, respectively. Pesticide application happened in the morning except for Visit 5, in which pesticide was applied at 3 p.m. The temperature inside the sampling cart was 2–5°F higher than the interiors of the greenhouses.

DISCUSSION

Issues with the ESP

The ESP method successfully collected metalworking fluid mist on the substrate in previous studies and showed smaller evaporative loss compared to the combination of filter cassettes and sorbent tubes. [15,19,36,37] Volckens and Leith[38,39] later reported that electrostatic precipitators have the potential for chemical artifact formation, especially with chemicals containing double bonds in their structure. Reaction and degradation due to ozone and corona-related ions in ESPs has been reported in other literature. [40–42] Flushing around the corona wire with filtered air can reduce this artifact.[42,43]

Chlorpyrifos has one double bond (PS) and one pyridine ring (C_5H_5N) (Figure 3). While the pyridine ring is relatively stable due to a conjugated system of delocalized electrons, the phosphate part is more reactive and is the common part of organophosphate pesticides. Volckens and Leith found that particle-phase SVOCs collected on the substrate are more susceptible to ozone and corona-related ions than SVOCs in gas or particle phase.[38] That finding may explain why no chlorpyrifos was recovered from the substrates of the ESP while small amounts of chlorpyrifos were recovered from the OVS tubes connected to the ESP. A white trace was noted on the substrate of the ESP after every sample, which may be

a degradation product. In a future study, the end products of ozone oxidization might be identified using mass spectrometry.

Issues with the SADS

The major issues raised with the SADS are lower concentrations at T1 and T2 compared to that measured by XAD-2 OVS tube reference method, and non-realistic phase profile found in Visit 5 ($f_{particle}$ (T1) < $f_{particle}$ (T2)). The lower concentrations than those measured by the reference XAD-2 OVS tube method were only significant at T1 and not at T2 or T3. One possible reason for lowered concentrations could be the absorption of chlorpyrifos by the connecting material between the SADS and its XAD-2 OVS tubes. In the laboratory test of SADS using oil mist, the sampling media were charcoal tubes which can be connected almost directly to the outlets of SADS using a short Tygon tubing.[19] Due to the wide opening of the OVS tube, some extra interface between the tube and SADS is inevitable. A male piece of a quick disconnect couplings was inserted into the inlet of an OVS tube and then a short $\frac{1}{4}$-inch Tygon tubing connected between SADS and the disconnect. This connecting material was not replaced between sampling periods. Absorbed chlorpyrifos might be released into air when the concentrations decreased over time and this might explain higher particle fractions at T2 and T3.

Another artifact that can affect the SADS method is particle size distribution and existence of small-diameter particles. The experimentally determined 50% cutsize of SADS is 0.25 μm.[18] If the mass median diameter of aerosols is smaller than 1 μm, the bias due to the particles flowing to the vapor flow of SADs increases significantly.[18,19] Using the separation efficiency of SADS and the size distributions of particles inside the greenhouses in Figure 2, the authors estimated misclassification bias according to reference.[17] While the bias during pesticide application was less than 1%, the biases at T2 and T3 increased up to 10%. Particle fractions significantly greater than zero after 24 hr from application are likely a result of fine particles formed during application since a 0.1 μm aerodynamic particle falls only a few centimeters over this time period. This observation is consistent with the measured size distributions during application (Figure 2).

Factors Affecting Phase Profiles

The factors affecting the airborne pesticide concentrations and their phase distributions can be categorized as pesticide, application method, and environment. Pesticide factors include active ingredients and their contents, vapor pressures of each active ingredient, and type of formulations. Pesticides are designed in the following forms: emulsifiable concentrate solution; flowable, wettable powder; dry flowable, soluble powder; ultra-low-volume concentrate; low concentrate solution; aerosol; invert emulsion; dust; bait; granule; pellets; micro encapsulation; water-soluble packets; and impregnates.[44] Vapor pressures of each active ingredient and the formula are hardly expected to be the same. Application method factors include spray nozzle and equipment, application types, and time spans after application. Common equipment include hand dusters, rotary-type hand dusters, knapsack dusters, power dusters, compressed air sprayers, power sprayers, hand sprayers, knapsack sprayers, and mist blowers (fogger). Some of them can be used only for solid formulations.

The application/treatment type can be classified as follows: band, basal, broadcast, directed, sequential, serial, and spot.[44]

Factors contributed by the environment include greenhouse characteristics, ventilation, existence of other solid particles, types and water content of soil, crop characteristics, and meteorological conditions. Although the dimensions of greenhouses, temperature, and relative humidity were investigated, it was not possible to find a statistical association between them and chlorpyrifos concentrations due to a small number of data. The sampling sites of this study were limited to greenhouses in research facilities. Some factors might affect the phase distributions differently in commercial greenhouses due to the differences in greenhouse size and application rate.

Temperature and humidity are important factors affecting phase distributions and sampling. During Visit 5, pesticide was applied in the afternoon when temperature is at the peak of a day, which might explain why the particle fraction at T1 was the smallest and the particle fraction at T2 was the largest among Visits 3 to 6. Humidity might play a bigger role outside greenhouses, but it still is an important factor inside them.[32,45] Oxidative loading to aluminum substrate of the ESP is a function of relative humidity.[38] By competing with chemicals of interest, high humidity can reduce the adsorptive capacity of sorbent tubes.

In any future study, the number of sampling visits should be increased sufficiently to run statistical analysis, such as generalized linear model or analysis of covariance (ANCOVA). Those analyses will help to identify the attributing factors including temperature, humidity, application method, and other characteristics previously described in this section. A new connection method between SADS and OVS tubes should be considered. Sampling in commercial-scale greenhouses will be ideal to estimate the exposure levels of agricultural workers. Extending study sites to polytunnels and farm fields are possible. Polytunnel is a more common form of enclosed framing practice than greenhouses in some countries.

CONCLUSION

The phase distribution and the concentrations of each phase of semi-volatile organic compounds (SVOCs) are important in establishing strategies of exposure assessment, hazard control, and worker protection. The mechanisms of the worker protection method are different for each phase and different phases can influence the respiratory toxicity of certain chemicals (e.g., upper respiratory versus lower respiratory effects). This study attempted to compare two sampling methods capable of determining phase information to evaluate methods for sampling chlorpyrifos in greenhouses that might provide more useful information than the typical collection of all phases without separation. The electrostatic precipitator (ESP) appeared to be affected by formation of chemical artifacts and was excluded as a potential candidate method for phase profile sampling in this situation. Although the SADS with XAD-2 OVS tube sample collection underestimated the overall concentrations compared to the independent XAD-2 OVS tubes (NIOSH #5600 method), it separated vapors and particles and enabled estimation of the phase distribution of the semivolatile chlorpyrifos, even though the accuracy of phase separation and recovery could not be verified in the absence of a standardized procedure. Particle size distribution and

temperature / humidity are believed to be factors significantly affecting the phase distributions of semivolatile aerosols, but this could not be proven in this pilot study.

Acknowledgments

The authors thank Sid Soderholm at NIOSH and Matthew Crowley at the Environmental Protection Agency (EPA) for reviewing this work and for the two institutes, that provided access to their greenhouses.

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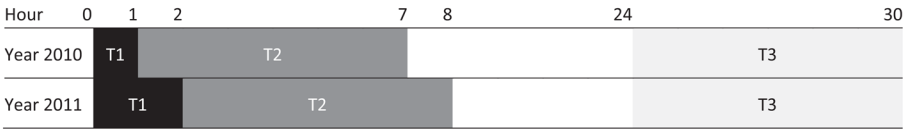

FIGURE 1.
Sampling time scheme in hour(s) after pesticide application.

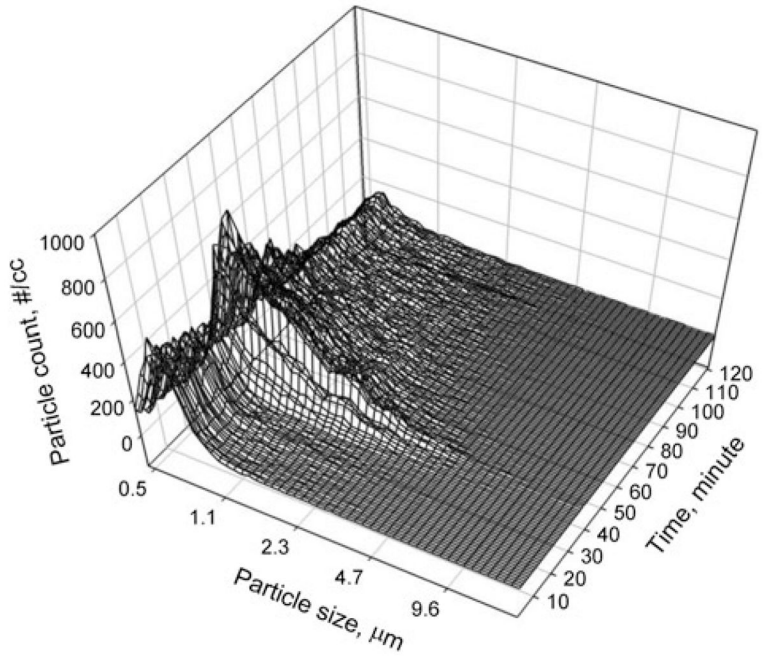

FIGURE 2.

Particle size distribution for the first 120 min of Visit 6. Pesticide application started at Time = 30 min and lasted for 25 min.

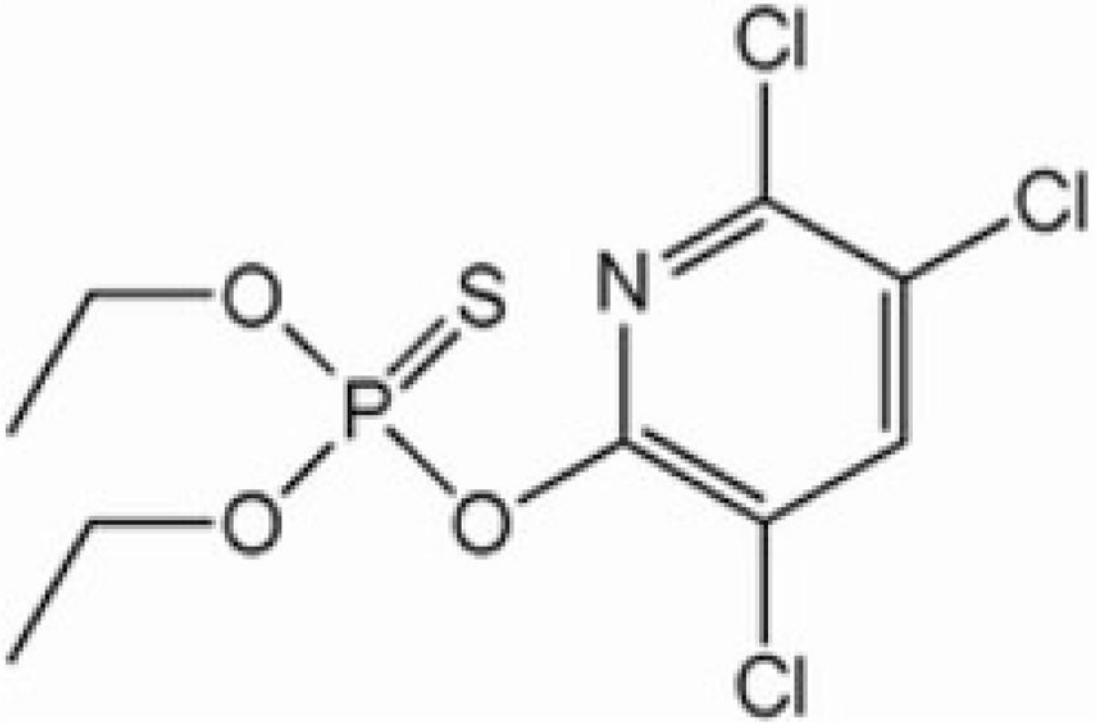

FIGURE 3.
Chemical structure of chlorpyrifos.

TABLE I

Summary of Data from Studies on Semivolatile Pesticide Exposure During Greenhouse Spraying or Polytunnel Spraying

Studies and pesticides	Measured values	Sampler
Adamis et al.[10]		Partly, two impingers in a series and containing abs. ethanol and partly, 0.8-μm-pore Gelman filter
Pirimiphos-methyl	0.007–0.165 mg/h	
Dimethoate	0.001–0.059 mg/h	
Permethrin	0.001–0.004 mg/h	
Al-Jaghbir et al. [24]		Glass impinger filled with ethylene glycol
Dimethoate	14.6–18.9 mg/day	
Aprea et al. [2001][21]		Fiberglass membrane filter
Omethoate	1.2–4.5 nmol/m^3	
Fenitrothion	0.4–2.6 nmol/m^3	
Tolclofos-methyl	0.4–17.4 nmol/m^3	
Aprea et al. [2002][25]		XAD-2 tubes
Chlorothalonil	3.14–11.57 μg/m^3	
Archibald et al. [1994][26]	Not detected	Glass tubes filled with florisil
Pirimicarb		
Archibald et al. [1995][27]	1.1–4.3 mg/m^3	Glass tubes filled with florisil
Pirimicarb	0.086–0.454 mg/m^3	
Deltamethrin		
Brouwer et al.[28]	(As total) 0.04–0.67 mg/m^3	XAD-2 tube with IOM sampling head for chlorothalonilIOM sampler with MCE filter for other pesticides
Chlorothalonil	1 ILV (mg/day) *A*	
Thiophanate-methyl	56 ILV (mg/day)	
Thiram	10 ILV (mg/day)	
Zineb	1 ILV (mg/day)	
Desi et al.[29]		Ethylene glycol monoethylether
Pyrethroids	Below LOD (1 μg/m^3) *B*	
Kangas et al.[30]		XAD-4 tubes
Mevinphos	4.8–76.9 μg/m^3	
Mestres et al.[31]		Glass columns filled with florisil
Dicofol	0.007–12 μg/m^3	
Deltamethrin	0.008–5.2 μg/m^3	
Siebers and Mattusch[23]		Tenax sorbent tubes
Dinocap	<0.2–2.3 μg/m^3	
Dichlofluanid	0.51–25 μg/m^3	
Parathion	0.53–28 μg/m^3	
Pirimicarb	<0.2–9.9 μg/m^3	
Stamper et al. [1988][32]	(greenhouse foggers)	Cylindrical polyurethane foam filter plug
Fluvalinate	0.3 μg/m^3	

Studies and pesticides	Measured values	Sampler
Chlorpyrifos	0.2 $\mu g/m^3$	
Ethazol	0.7 $\mu g/m^3$	
Stamper et al. [1989][33]	(drencher)	Cylindrical polyurethane foam filter plug
Fluvalinate	1.5–11.7 $\mu g/m^3$	
Chlorpyrifos	2.9–15.8 $\mu g/m^3$	
Ethazol	34.3–137 $\mu g/m^3$	
Chlorothalonil	6.5–33.4 $\mu g/m^3$	
Stamper et al. [1989][34]	(handgunners)	Cylindrical polyurethane foam filter plug
Fluvalinate	2–12 $\mu g/m^3$	
Chlorpyrifos	9–75 $\mu g/m^3$	
Ethazol	55–113 $\mu g/m^3$	
Dicofol	5 $\mu g/m^3$	
Stamper et al. [1989][35]	(applicator)	Cylindrical polyurethane foam filter plug
Fluvalinate	<0.3–2 $\mu g/m^3$	
Chlorpyrifos	8–27 $\mu g/m^3$	
Captan	6–15 $\mu g/m^3$	
Chlorothalonil	9 $\mu g/m^3$	

[A] ILV: indicative limit value.

[B] LOD: limit of detection.

TABLE II

Information on Sampling Visits

Visit	Year and sampling scheme (Figure 2)	Sampling site	Pesticide application equipment	Application rate (active ingredient)	Temperature Inside/Outside (°F)
1	2010	MN	DrammMSO Sprayer	30 cc/hr	60s/70s
2				120 cc/hr	50s/50s
3		MD	DrammMSO Sprayer	18 cc/hr	80s/70s
4				14 cc/hr	80s/70s
5	2011	MD	DrammMSO Sprayer	25 cc/hr	90s/80s
6				18 cc/hr	90s/80s

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TABLE III

Overall Concentrations of Chlorpyrifos in $\mu g/m^3$

	T1			T2			T3		
Visit	**SADS** [A]	**ESP**	**OVS**	**SADS**	**ESP**	**OVS**	**SADS**	**ESP**	**OVS**
1	6.1	<LOD [B]	11.7	0.4	< LOD	0.6	0.1	0.1	0.1
2	13.5	0.5	31.0	0.3	0.1	0.4	0.1	< LOD	0.2
3	34.2	—	46.3	13.9	—	20.6	0.7	—	0.6
4	93.9	—	126.9	54.0	—	76.7	2.6	—	2.6
5	61.9	—	85.5	7.6	—	9.7	1.1	—	1.3
6	131.9	—	186.6	46.3	—	57.9	2.6	—	1.9

[A] The overall concentrations for SADS have been calculated using Eq. (3).

[B] LOD: limit of detection was 0.05 μg/sample.

TABLE IV

Chlorpyrifos Concentrations in Each Phase in $\mu g/m^3$ and Fraction of Particle Concentration Calculated Using Eqs. (1), (2), and (4)

	T1			T2			T3		
Visit	C_{vapor}	$C_{particle}$	$f_{particle}$	C_{vapor}	$C_{particle}$	$f_{particle}$	C_{vapor}	$C_{particle}$	$f_{particle}$
1	< LOD	6.1	—	< LOD	0.4	—	< LOD	0.1	—
2	< LOD	13.5	—	< LOD	0.3	—	< LOD	0.1	—
3	9.0	25.9	0.74	10.5	3.5	0.25	1.18	< LOD	0.00
4	44.6	50.6	0.53	46.6	7.4	0.14	2.5	0.1	0.04
5	39.9	22.0	0.36	4.4	2.9	0.40	0.8	0.2	0.20
6	76.1	49.3	0.39	34.8	12.3	0.33	2.0	0.5	0.19